BIODIESEL FROM VARIOUS VEGETABLES AND TALLOW OILS

ATIQAH BINTI NAFSUN

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Faculty of Mechanical Engineering
UNIVERSITI MALAYSIA PAHANG

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ABSTRACT

This thesis deals with Biodiesel from various vegetables and tallow oils. The objective of this thesis is to produce the biodiesel from various feedstocks which are palm oil, corn oil, chicken fat oil, soybean oil, sunflower oil and waste cooking oil and also to analyze the physical properties each of biodiesel oil. The thesis describes the proper biodiesel extraction process, using proper catalyst and solvent in order to get the biodiesel physical properties standard of B100, ASTM6571. The studies of physical properties of biodiesel that are involved in this thesis consist of density, viscosity, cetane number, flash point, cloud and pour point and also acid value. As result, we observed that palm oil has a nearest physical properties standard, ASTM6571. We compared these six different feedstock physical properties with some literature. As for the recommendation, conduct engine testing operating with various biodiesel and also perform one-dimensional simulation of internal combustion engine which operating with simulation such as GT-Power.
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ABSTRAK

Tesis ini berkaitan dengan Biodiesel dari pelbagai sayur-sayuran dan minyak lemak haiwan. Objektif tesis ini adalah untuk menghasilkan biodiesel daripada pelbagai bahan mentah iaitu dari minyak sawit, minyak jagung, minyak, lemak ayam, minyak kacang soya, minyak bunga matahari dan sisa minyak masak dan juga untuk menganalisis sifat fizikal setiap minyak biodiesel. Tesis ini menerangkan pengekstrakan proses biodiesel yang betul, menggunakan pemangkin yang betul dan pelarut untuk mendapatkan sifat-sifat biodiesel mengikut sifat-sifat fizikal piawaian B100, ASTM6571. Kajian sifat fizikal biodiesel yang terlibat di dalam tesis ini terdiri daripada ketumpatan, kelikatan, nombor cetana, takat kilat, awan dan takat tuang dan juga nilai asid. Hasilnya, kami memerhatikan bahawa minyak sawit mempunyai sifat-sifat fizikal yang terdekat dengan sifat-sifat fizikal standard, ASTM6571. Kita membandingkan sifat fizikal yang berbeza untuk setiap bahan mentah yang berbeza. Bagi syor itu, menjalankan operasi pengujian enjin dengan pelbagai jenis biodiesel dan juga melaksanakan satu dimensi simulasi enjin pembakaran dalaman yang beroperasi dengan simulasi seperti GT-Power.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Material
HHV	Higher Heating Value
B5	5 % Biodiesel, 95 % Diesel
B20	20 % Biodiesel, 80 % Diesel
B100	100 % Biodiesel
FFA	Free Fatty Acid
WCO	Waste cooking oil
SANS	Small-angle neutron scattering
FFEM	Freeze-fracture electron microscopy
KOH	Potassium Hydroxide
NaOH	Sodium Hydroxide
HC	Hydrocarbons
PAHs	Polycyclic aromatic hydrocarbons
CO	Carbon Monoxide
CO_2	Carbon Dioxide
NOx	Nitrogen Oxide
EGR	Exhaust-gas recirculation
CFPP	Cold Filter Plugging Point
EEB	European Environmental Bureau
BSFC	Brake specific fuel consumption
BSEC	Brake specific energy consumption
SOx	Sulfur dioxide

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

In this recent year, the world was hit by energy crisis. Nowadays, the increasing demand for energy and the diminishing of crude petroleum oil resources has lead to the research for a new alternative energy. The global concern about the petroleum resources was limited reserves and only concentrated in certain region in the world. Many researchers suggest that the sources reserve is only last for the next few decades. As we know that most of the transportation vehicles used fossil fuel such gasoline, liquid petroleum oil and diesel fuel. About 98 % of carbon emissions result from fossil fuel combustion. Alternatives energy such as hybrid technology requires extra modification to the vehicles engine. Beside the higher cost were needed, the time to develop is much longer, and inappropriate in short term replacement to fossil fuel.

Every sector across the globe needed energy, an energy that can be renewed and more important is a climate friendly that won't affect our green earth and human health as well. Transportation is one of the sectors that contribute to the energy application. Nowadays, the awareness about the energy losses and energy production are being considerate. There are some energy production developed from biomass, biogas, bioethanol, biohydrogen and biodiesel. The word bio significantly shows that the energy is safe for all of us. Among of them, biodiesel is a huge energy competitor that can go far. In term of production and application, biodiesel win a heart of researchers and leaders all over the world. Biodiesel is safely produced and handle, safely for our earth and easy to produce. The production of biodiesel will help the economic growth and help the development of the agriculture sector. It will help in increasing the exchange money rate and enhance the living standard particularly.

Biodiesel found out to be the best substitute for crude petroleum oil because it is renewable and sustainable. Moreover it is an environmental friendly fuel. The energy demand was fulfilled by conventional energy sources such as coal and fossil. Thus, renewable biodiesel replace the utilization of non renewable fossil fuels and coal that were limited.

Biodiesel is an alternative fuel for diesel engines that is produced by chemical reaction between a vegetable oils and fat oils with an alcohol. The reaction require a catalyst, whether acidic, alkaline catalyst or enzyme catalyst. Usually a strong alkali base, such as sodium or potassium hydroxide used in biodiesel production and produced a new compounds called methyl esters or ethyl esters. These fatty acid esters are also known as biodiesel. The combustion resulted by using biodiesel shown no decreasing in performance, instead its produce more clean exhaust emission. Three advantages that biodiesel has been recognize as major renewable energy resources are because its renewable resources that could be sustainable developed in the future, environmental friendly and give significant economic potential that can be developed in the near futures. With these advantages, biodiesel promises a bright future in the fuel industry.

In Malaysia, the biodiesel was accepted and known widely. The National Biofuel Policy was launched by government in 2006. The policy aimed to reduce country import bill and also promoting the further demand for palm oil for biodiesel production. The demand for biofuel in Europe is projected to increase from 3 million tonne in 2005 to 10 million tonne in 2010 (The National Biofuel Policy, 2006). Malaysia has aims to become a global leader in biodiesel production because Malaysia has a large palm oil plantation and the second exporter for palm oil worldwide behind Indonesia. In June 2010, Malaysia considers cutting a diesel subsidy to make the biodiesel industry more attractive after production of the alternative fuel virtually ground to a halt. Because of the subsidy on diesel, it has somewhat distorted the price for biodiesel to be utilized.

Palm oil is one of the seventeen major oil traded in the global edible oil and fats market. Palm oil is consumed worldwide in more than 100 countries in the world (MPOC, 2007). Malaysia is a larger producer of palm oil worldwide and contributes 29% of biodiesel production from the palm oil. Government planned to provide a fund to palm oil producer across the country. One of them is Petronas Dagangan Berhad. This fund will growth the interest for palm oil company to set up new facilities in term of production and research. The rising cost for palm oil producing will increase the biofuels manufacturing process. Yet, the government should take a concern to give the subsidy to those who were involved.

1.2 PROBLEM STATEMENT

Malaysia is known as the second exporter for palm oil worldwide behind Indonesia. Thus, Malaysia has the potential to lead the way in biofuel production capitalizing on its vast production of agricultural products and by-products. This will contribute in utilizing local resources for biofuel, exploiting local technology to generate energy for the transportation and industrial sectors, and paving the way for exports of biofuel. The price of biodiesel is much higher compare to conventional diesel makes it is less chosen by the customer. Thus the aim of this project is to produce biodiesel as diesel substitute with minimum cost with potential to be commercialized. The sensitivity of oil palm price resulted in instability of oil palm price. The higher prices of crude petroleum oil will shift the market trend favorable towards the palm oil. Thus, the high market demand of palm oil makes the prices more volatile. Even though the price of palm oil is much cheaper than crude petroleum oil, Malaysia government gives subsidized to petroleum oil in transportation sector resulted in lower prices compare to biodiesel. The main reason of high prices in production of biodiesel is because of its raw material. Thus, using waste cooking oil as raw material will make the biodiesel price more comparable than subsidized petroleum diesel. The availability, cost and the continuity are the main criteria for good raw material. The easy availability of waste cooking oil and continuity of supply make it as a good choice of raw material. Single steps transesterification process will be used in synthesizing waste cooking oil to methyl ester. Single steps transesterification process provide less time in reaction, lower temperature and pressure, gives a better yield and hence will result in less cost of production. The high content of free fatty acid in waste cooking oil need to be synthesize using homogenous catalyst. Even though the use of homogenous catalyst resulted in higher formation of soap, homogenous catalyst provides shorter reaction time compare to heterogeneous catalysts. Powdered sodium methoxide is used as homogenous catalyst in this experiment and methyl alcohol will use as alcohol solvent because of its price is cheaper among other alcohol solvent.

1.3 PROJECT OBJECTIVES

The objective of this project is to produce biodiesel from various vegetable oil such as palm oil, coconut oil, corn oil, olive oil, sunflower oil, peanut oil and from animal fats such as chicken, goat and cow fat.

1.4 SCOPE OF THE STUDY

This research is an experimental analysis study in a production of biodiesel from palm oil, corn oil, soybean oil, sunflower oil, waste cooking oil and animal fats from chicken as the feedstock. In order to achieve the project objective, three scopes have been identified to be studied. These three scopes are:

i. Produces biodiesel with a various feedstock

ii. Measure physical properties of biodiesel produced

iii. Analysis and report writing

CHAPTER 2

LITERATURE REVIEW

2.1 OVERVIEW

Biodiesel is an alternative fuel for diesel engines. It chemically produced by reacting vegetable oil or fat oil with alcohol as a solvent. The most frequently alcohol used is acyl receptor particularly methanol and lesser extent which is an ethanol. The concept of using biodiesel in diesel engines originated by diesel engine inventor, Rudolf Diesel at the World Exhibition at Paris in 1900 as he used peanut oil as a fuel (Agarwal, 2001) However, due to the then-abundant supply of petroleum crude oil, research and development activities were not seriously pursued. Recently after the world having a energy crisis, the dramatic increase price of crude petroleum oil, the increasing concern regarding environment issues that is related to the greenhouse gas effect emission, the new health and safety consideration are forcing the search for energy sources and alternative ways in order to prevent all of these problems.

Biodiesel production is very modern and technological area for researchers due to the relevance that is winning every day. The commercialization of biodiesel in many countries around the world has been accompanied by the development of standards to ensure the high product quality and user confidence. The commonly standard use for biodiesel production is American Society for Testing and Materials, ASTM6751 and European standard EN14214, which was developed from previously existing standards in European countries (Knothe, 2005)

The American Society for Testing and Material (ASTM) defined biodiesel fuel as monoalkyl esters of long chain fatty acids derived from renewable lipid feedstock such as vegetable oils or animal fats. Biodiesel fuels are characterized by their cetane number, density, viscosity, cloud and pour points, flash point, copper corrosion, ash content, distillation range, sulfur content, carbon residue, acid value, free glycerine content, total glycerine content and higher heating value (HHV). The viscosity values of vegetable oils decreases sharply after transesterification reaction (Sharma, 2008). Biodiesel is the only alternative fuel that can be used in diesel engine directly without any modification of engine. Biodiesel fuel attracting more attention worldwide while introducing a blending component or direct replacement for diesel fuel in diesel vehicle engines (Demirbas, 2009). When blended with diesel fuel the designation indicates the amount of B100 in the blend, e.g. B20 is 20 % of B100 and 80 % diesel fuel and B5 is 5 % B100 in diesel fuel. Usually B20 is used because it is nearly all the diesel equipment are compatible to used with. These lower blends do not require any diesel engine modification compare to B100 that sometimes need a little modification. Table 2.1 shows the ASTM standard specification for neat biodiesel, B100 to be used in diesel engine.

Table 2.1 : ASTM standard specification for neat biodiesel B100

Source : (Yusuf et al., 2011)

Property	Test Method	ASTM D975 (petroleum diesel)	ATSM6751 (biodiesel B100)
Flash point	D93	325K min	403K
Water and sediment	D2709	0.05 max vol.%	0.05 max vol.%
Kinematic viscosity (at 313K)	D445	1.3-4.1 mm^2/s	1.9-6.0 mm^2/s
Sulfated ash	D874	-	0.02 max wt.%
Ash	D482	0.01 max wt.%	-
Sulfur	D5453	0.05 max wt.%	-

Sulfur	D2622/129	-	0.05 max wt.%
Copper-strip corrosion	D130	No.3 max	No.3 max
Cetane number	D613	40 min	47 min
Aromaticity	D1319	35 max vol.%	-
Carbon residue	D4530	-	0.05 max mass%
Carbon residue	D524	0.35 max mass%	-
Distillation temp. (90% volume recycle)	D1160	555K min-611K max	-

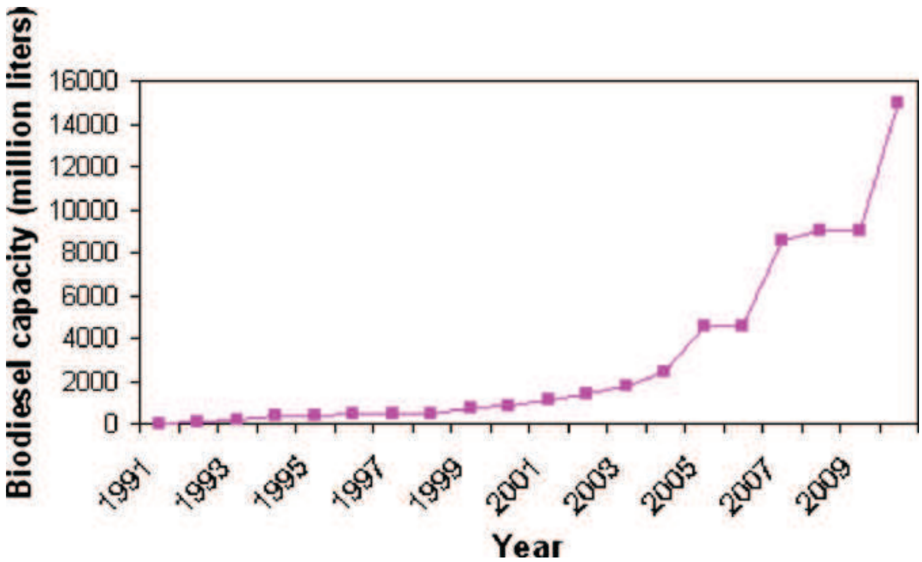

Figure 2.1 : World biodiesel capacity, 1991–2010

Source : (International Energy Agency).

2.1 RENEWABLE SOURCES FOR BIODIESEL PRODUCTION

2.1.1 Animal fats

Another group of feedstock for biodiesel production is fats derived from animals. Animal fats used to produce biodiesel include tallow (Oner, 2009), white grease or lard (Lu, 2007), and chicken fat (Guru, 2010). Compared to plant crops, these fats frequently offer an economic advantage because they are often priced favorably for conversion into biodiesel (Wen, 2009). Moreover, it has some advantages such as high cetane number, non-corrosive, clean and renewable properties (Guru, 2009). Animal fats has a low free fatty acid (FFA) and water, but there is a limited amount of these oils available, meaning these would never be able to meet the fuel needs of the world (Sheedlo, 2008).

2.1.2 Edible oil

Biodiesel has been mainly produced from edible vegetable oils all over the world. Currently, more than 95 % of the world biodiesel is produced from edible oils which are easily available on large scale agricultural industry country (Gui, 2008). However, continuous and large scale production of biodiesel from edible oils has recently arise a concern because they are competing with food materials. There are concerns that biodiesel feedstock may compete with food supply in the long term (Refaat, 2010). Figure 2.2 shows the biodiesel production by vegetable oil globally.

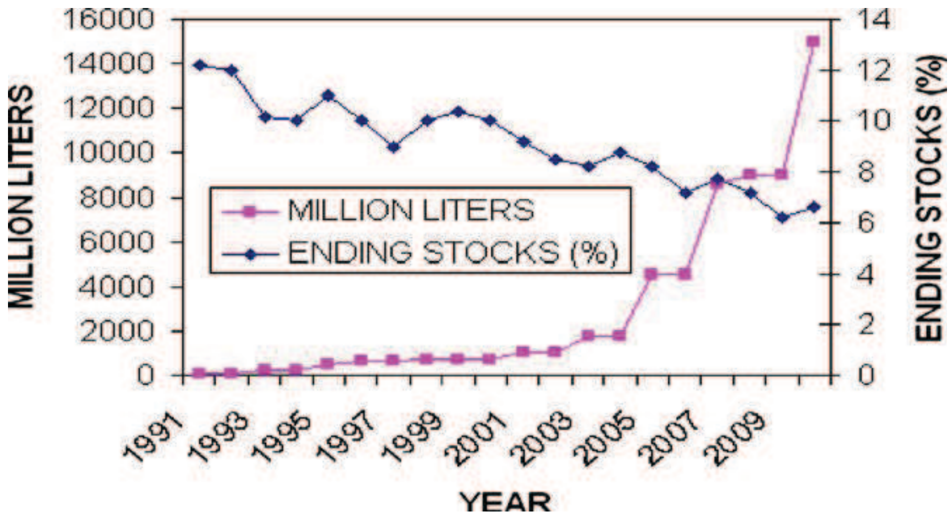

Figure 2.2 : Global vegetable-oil blending stock and biodiesel production

Source : Gui, M.M. et al., (2008).

Currently, biodiesel is prepared from conventionally grown edible oils such as rapeseed, soybean, sunflower and palm oils thus leading to the alleviate food versus fuel issues (Anwar, 2010). About 7 % of global edible vegetable oil supplies were used for biodiesel production in 2007 (Mitchell, 2008). The rapidly growing world population needs a food and the raise consumption of biodiesel cause a major problem.

2.1.3 Non-edible oil

Non edible plant oils have been found out to be promising crude oils for biodiesel production. The used of non-edible oils compared to edible oils is very significant in developing countries because of the tremendous demand for edible oils as a food. Edible oil are far too expensive to be used as a fuel (Pramanik, 2003). The production of biodiesel using non-edible oil has been investigated and carried out for the last few years. Some of these non-edible oilseed crops include jatropha tree (Jatropha curcas) (Tiwari, 2007), karanja (Pongamia pinnata) (Naik, 2008), tobacco seed (Nicotiana tabacum L) (Veljkovic, 2006), ricebran (Sinha,2008),mahua (Madhuca indica) (Raheman, 2007), neem (Azadirachta indica) (Rao, 2008), rubber plant (Hevea brasiliensis) (Ramadhas, 2005), castor (Sousa, 2010), linseed, and micro-algae (Demirbas, 2009).

2.1.4 Waste cooking oil

The biodiesel production from waste cooking oil (WCO) has substitute the depletion of petroleum diesel. It is one of the measures for solving the problems of environment pollution and energy shortage. Waste cooking oil is more cheaper compared to other biodiesel feedstock. Moreover, the raw material is easy to get and the price is 2-3 times cheaper than virgin vegetable oils. Waste cooking oil is categorized based on its FFA. The amount of WCO generated in each country is different depending on overall country vegetable oil used. Management of WCO is a quite a challenge because of its disposal creates a huge problem and possible of contamination of the water and land resources.

2.3 THE PRODUCTION OF BIODIESEL

There are many considerable efforts done to develop vegetable-oil derivatives that approximate the properties and performance of hydrocarbon based diesel fuels. The problem arise with substituting triglyceride mostly associated with (i) higher viscosity; (ii) low stability against oxidation(polymerization reactions); and (iii) low volatility which can be influence the forming of amount of ash due to incomplete combustion (Robles-Medina, 2005). Four ways are identified in order to overcome these problems in biodiesel production.

2.3.1 Direct use and blending

Vegetable oil can be mixed with diesel fuel and can be used directly for running in the diesel engine. The successful experimental blending of vegetable oil with diesel fuel has been done by various researchers. A blend of 95 % filtered used cooking oil and 5 % diesel in 1982 used in a diesel fleet. In 1980, Caterpillar Brazil Company used pre-combustion chamber engines with a mixture of 10 % vegetable oil to maintain total power without any modification to the engine. Thus, a blend of 20 % oil and 80 % diesel was found to be successful and known as B20. Pramanik found that a 50 % blend of Jatropha oil can be used in diesel engines without any major operational difficulties but further study is required to determine the long-term durability of the engine. The direct use of vegetable oils or the use of oil blends have generally been considered to be unsatisfactory and impractical for both direct and indirect diesel engines. The high viscosity, acid composition, free fatty-acid content, gum formation due to oxidation, polymerization during storage and combustion, carbon deposits and lubricating-oil thickening are the obvious problems.

The use of 100 % vegetable oil was also proven and it require a possible minor modification to the fuel system. There are some major problems that have been associated with the use of pure vegetable oils as fuels in compression ignition engines; it is mainly due to the increased viscosity. Micro-emulsification, pyrolysis and transesterification have been used as remedies to solve these problems encountered due to high fuel viscosity (Ramadhas, 2004).

2.3.2 Microemulsion

Microemulsion is isotropic, clear or translucent, thermodynamically stable dispersions of oil, water, surfactant, and often a small amphiphilic molecule, called a co surfactant. It is made of vegetable oils with an ester and dispersant (co solvent), or of vegetable oils, an alcohol and a surfactant, with or without diesel fuels. Because of their alcohol contents, microemulsions have lower volumetric heating values than diesel fuels, but these alcohols have high latent heats of vaporization and tend to cool the combustion chamber, which reduces nozzle coking. A microemulsion of methanol with vegetable oils can perform nearly as well as diesel fuels. The use of 2-octanol as an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil has been demonstrated, the viscosity was reduced to 11.2 Cst at 25 ^{o}C. The reported engine tests on a microemulsion consisting of soybean oil: methanol: 2-octanol: cetane improver (52.7: 13.3: 33.3: 1) indicated the accumulation of carbon around the orifices of the injector nozzles and heavy deposits on exhaust valves (Srivasta, 2000)

Jesus et al. introduced a microemulsion used method for the determination of sodium and potassium in biodiesel using a water-in-oil emulsion process for biodiesel production from various and different sources such as soybeans, sunflower oil, animal fat and other vegetable oils. Wellert et al. studied the phase behavior of a microemulsion and a bi-continuous phase was identified using small-angle neutron scattering (SANS) and freeze-fracture electron microscopy (FFEM). The influence of choice of co-surfactant on the structural parameters was also studied.

2.3.3 Thermal cracking (Pyrolysis)

Pyrolysis is the conversion of an organic substance into another by means of heat or by no heat in the presence of a catalyst in the absence of air or oxygen. The material used for pyrolysis can be vegetable oils, animal fats, natural fatty acids and methyl ester of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum. Many investigators have studied the pyrolysis of triglycerides to obtain products suitable for diesel engines. Thermal decomposition of triglycerides produces alkanes, alkenes, alkadienes, aromatics and carboxylic acids (Pramanik, 2008)

2.3.4 Transesterification

Transesterification is a reaction process of triglyceride with an alcohol with the presence of catalyst usually acid and alkaline catalyst to produce fatty acid esters and glycerol. This process has been widely used to reduce the high viscosity of triglycerides. Methanol and ethanol widely used because of cheaper price easily dissolve and it can react quickly compared to other alcohol solvent. A catalyst played along to improve the transesterification process in term of reaction rate and yield product. Normally, alkaline-base catalyst is used in transesterification process for large scale biodiesel production because alkaline metal such as potassium hydroxide, KOH and sodium hydroxide, NaOH are more effective than acid-base catalyzed transesterification process. Figure 2.3 shows the transesterification process of triglycerides with alcohol solvent.

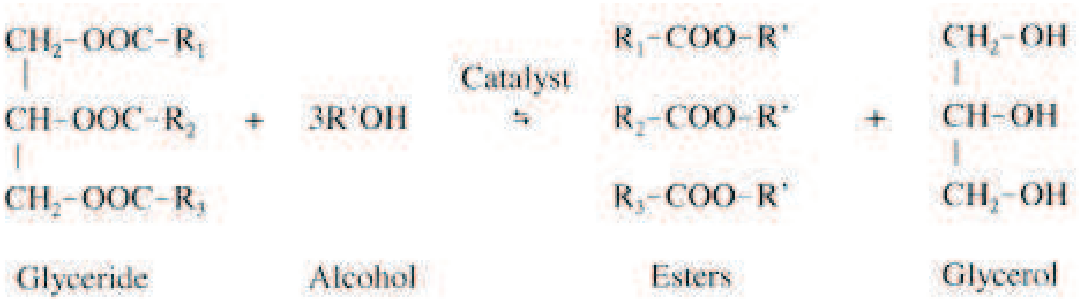

Figure 2.3: Transesterification process of triglycerides with alcohol.

Source: Xu, G. et al., (2003)

From figure basically the transesterification is a reversible process. It can be either triglyceride convert to diglyceride or shifted diglyceride to triglyceride. Alcohol acts as a solvent and reacting with the vegetable oil and fat oil. As for catalyst it is help to improve reaction rate and yield process.

2.4 TRANSESTERIFICATION

2.4.1 Reaction and mechanism

In the transesterification process, triglycerides are firstly converted to diglycerides, then monoglycerides and lastly glycerol. Transesterification of triglycerides produce fatty acid alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. The mechanism of transesterification is described in Figure 2.4, the reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In the presence of excess alcohol, the foreword reaction is pseudo-first order and the reverse reaction is found to be second order. It was also observed that transesterification is faster when catalyzed by alkali.

$$\text{Triglyceride} + R^1OH \rightleftharpoons \text{Diglyceride} + RCOOR^1$$

$$\text{Diglyceride} + R^1OH \rightleftharpoons \text{Monoglyceride} + RCOOR^1$$

$$\text{Monoglyceride} + R^1OH \rightleftharpoons \text{Glycerol} + RCOOR^1$$

Figure 2.4: General equation for transesterification of triglycerides

Source: Kambiz, T.A. et al., (2011)

The mechanism of alkali catalyzed transesterification is described in Figure 2.5. The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule, which results in the formation of a tetrahedral intermediate. The reaction of this intermediate with an alcohol produces the alkoxide ion in the second step. In the last step, the rearrangement of the tetrahedral intermediate gives a result to an ester and alcohol.

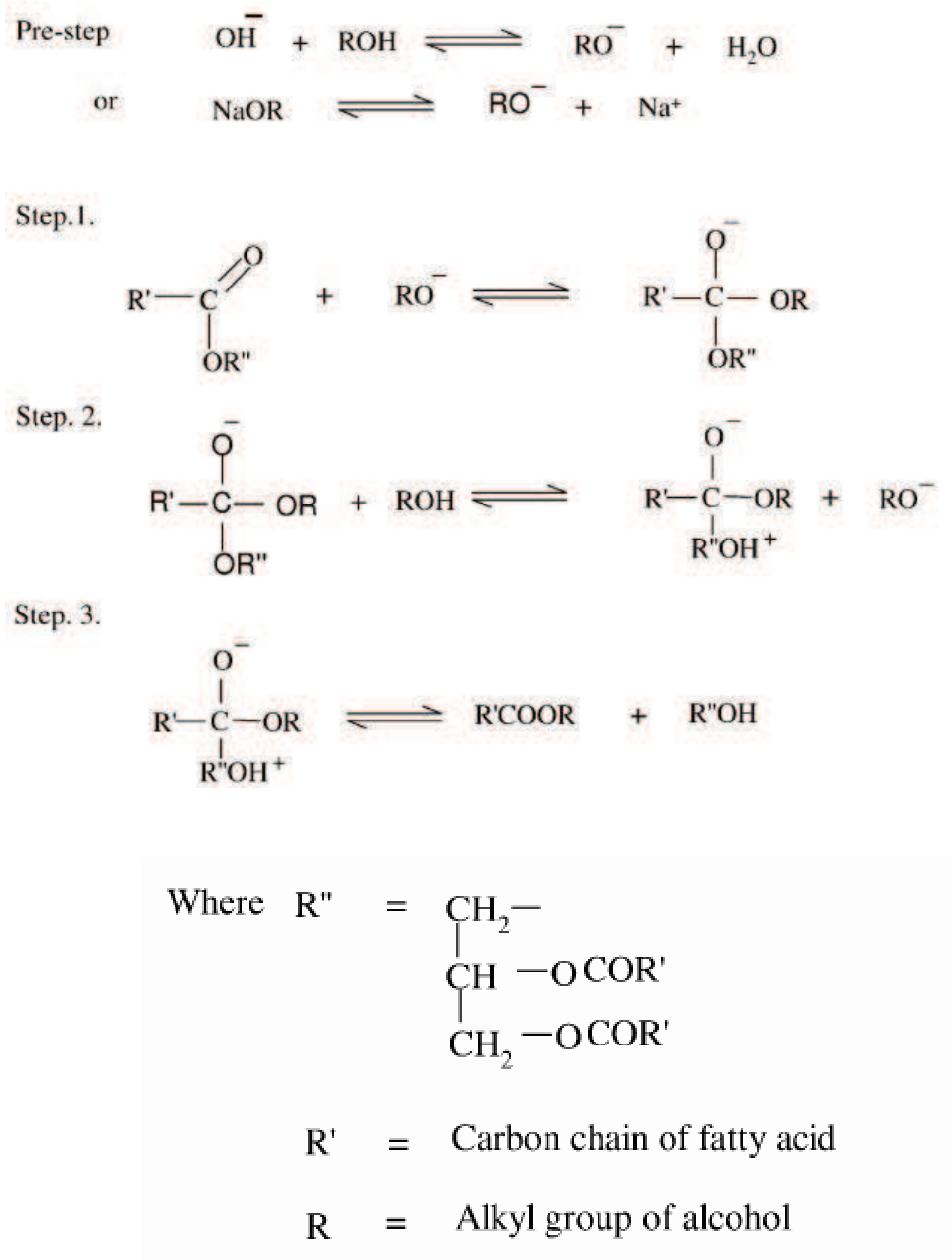

Figure 2.5: Mechanism of base catalyzed transesterification.

Source : Kambiz, T.A. et al., (2011)